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CaCuMn₆O₁₂ vs. CaCu₂Mn₅O₁₂: a comparative study

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The ferrimagnetic compounds Ca(Cu_xMn_{3-x})Mn₄O₁₂ of double distorted perovskites AC₃B₄O₁₂ family exhibit a rapid increase of the ferromagnetic component in magnetization at partial substitution of square coordinated (Mn³⁺)_C for (Cu²⁺)_C. In transport properties this is seen in a change of semiconducting type of resistivity for the metallic one. The evolution in magnetic properties of Ca(Cu_xMn_{3-x})Mn₄O₁₂ is driven by strong antiferromagnetic exchange interaction of (Cu²⁺)_C with octahedra coordinated (Mn^{3+/4+})_B. The competing interactions of (Mn³⁺)_C with (Mn^{3+/4+})_B lead to the formation of non – collinear magnetic structures which can be aligned by magnetic field.

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Nowadays, alongside with continuing studies of colossal negative magnetoresistance in traditional manganese – based perovskites this effect is actively investigated in more exotic systems like Cu – doped spinels FeCr₂S₄ or pyrochlore Tl₂Mn₂O₇ [1, 2]. The final goal of these studies is a magnetoresistance of about few percents at elevated temperatures. Among the most promising candidates for that are the double distorted perovskites of general formula Ca(Cu_xMn_{3-x})Mn₄O₁₂. The rich physics in these compounds follows from multiple and competing interactions of different magnetoactive ions in different crystallographic positions.

These compounds belong to the structural type AC₃B₄O₁₂ of cubic symmetry *Im* $\bar{3}$ [3]. The A position is twelve – coordinated and can be occupied by any large size ion independent of its valence state (e.g. Na⁺, Ca²⁺, Y³⁺, or Th⁴⁺). The C position is square coordinated and is preferable for the Jahn–Teller ions (e.g. Cu²⁺, Mn³⁺). The B position is octahedrally coordinated and can be occupied by both Mn³⁺ and Mn⁴⁺ ions. The tilted corner sharing octahedra BO₆ form the rigid perovskite framework while the CO₄ squares are not connected to each other.

Magnetic and transport properties of AC₃B₄O₁₂ compounds with various compositions were the subject of several experimental and theoretical studies [4–13]. At substitution of Cu²⁺ for Mn³⁺ in C position the Curie temperature within the Ca(Cu_xMn_{3-x})Mn₄O₁₂ family rapidly increases reaching $T_C = 355$ K in CaCu₃Mn₄O₁₂ [6]. This process is accompanied by a change of manganese valence state in B position from Mn³⁺ to Mn⁴⁺.

In Ca(Cu_{2.5}Mn_{0.5})Mn₄O₁₂ a non – collinear magnetic structure was established in neutron scattering measurements [11, 12]. It was found, that the magnetic moments of Cu²⁺ in C position are oriented antiparallel to the magnetic moments of Mn^{3+/4+} in B position, while the magnetic moments of Mn³⁺ in C position are tilted from this alignment. The evolution of physical properties within the Ca(Cu_xMn_{3-x})Mn₄O₁₂ family with the increase of copper content is not fully investigated. In particular, the mechanisms responsible for the formation of collinear or non – collinear magnetic structures are not clarified yet. In this work we report on a comparative study of two isostructural compounds CaCuMn₆O₁₂ and CaCu₂Mn₅O₁₂ whose properties in a sense differ qualitatively.

In this study the magnetization, specific heat and resistivity were investigated on ceramic samples of the title compounds. The samples were obtained by aerosol spray pyrolysis of nitrates solutions with subsequent annealing at 850 °C for 48 hours. The magnetization up to 5 T in a temperature range 2–350 K was measured by a MPMS “Quantum Design” magnetometer. The magnetization in fields up to 50 T was measured in a pulsed field facility. The specific heat was measured in a quasadiabatic relaxation type “Termis” calorimeter in a temperature range 5–273 K. The resistivity was measured by a standard four – probe method.

The temperature dependences of magnetization M in CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2) taken at $H = 0.1$ T are shown in Fig.1. Both curves present ferromagnetic – like upturns at $T_{C1} = 190$ K and $T_{C2} =$

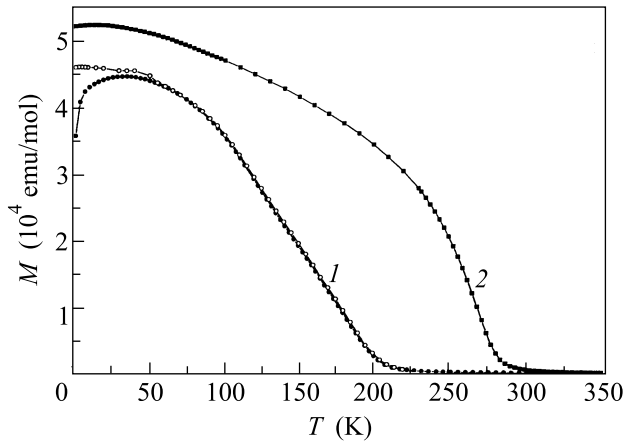


Fig.1. The temperature dependence of magnetization of CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2), $H = 0.1$ T

= 295 K for former and latter compounds, respectively. As it is shown for CaCuMn₆O₁₂, a ZFC–FC hysteresis of magnetization is observed.

The field dependences of magnetization in CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2) measured at $T = 5$ K in pulsed magnetic field are shown in Fig.2. These dependences differ qualitatively. In both

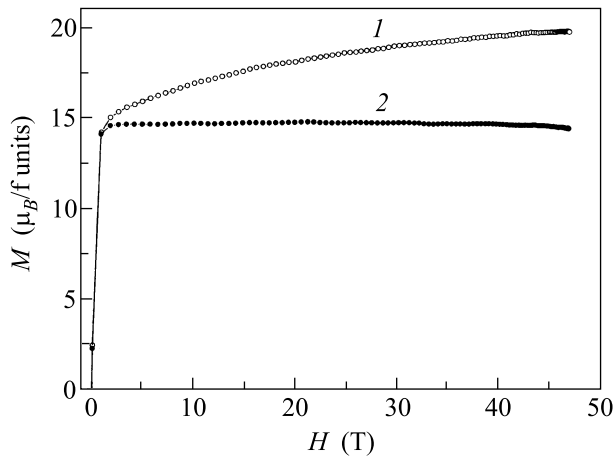


Fig.2. The magnetization curves of CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2) at $T = 5$ K

compounds, the magnetization rapidly increases in weak magnetic field reaching values of about $15 \mu_B$ per formula unit, but for further increase of magnetic field M_1 continually rises, while M_2 saturates. M_1 saturates at about 45 T reaching the value of about $20 \mu_B$ per formula unit.

The temperature dependences of specific heat C in CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2) are shown in Fig.3. The C vs. T dependences are in good correspondence with the M vs. T dependences. At $T < T_{C1}$, C_1

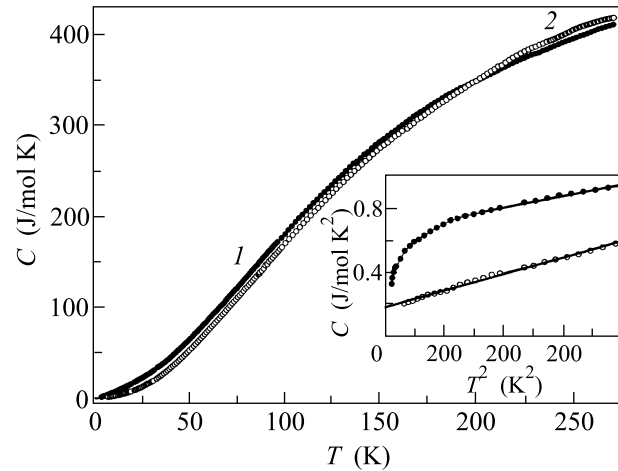


Fig.3. The temperature dependence of specific heat in CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2)

clearly exceeds C_2 , which indicates dominance of magnetic specific heat contribution in CaCuMn₆O₁₂. At $T > T_{C1}$, the opposite situation is realized, i.e. C_2 exceeds C_1 . In this temperature range the magnetic specific heat contribution exists only in CaCu₂Mn₅O₁₂. The C/T vs. T^2 dependences shown in the inset to Fig.3 indicate that the specific heat of CaCu₂Mn₅O₁₂ includes the electronic contribution $C_{el} = \gamma T$ shown with black line unlike that of CaCuMn₆O₁₂. The value of $\gamma = 0.164 \text{ J/mol} \cdot \text{K}^2$ was used to estimate the charge carriers concentration which amounts at low temperatures $\sim 10^{19} \text{ cm}^{-3}$.

Most clearly the difference in physical properties of CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2) is seen in the temperature dependences of resistivity shown in Fig.4. While the ρ_1 vs. T dependence is of semiconducting

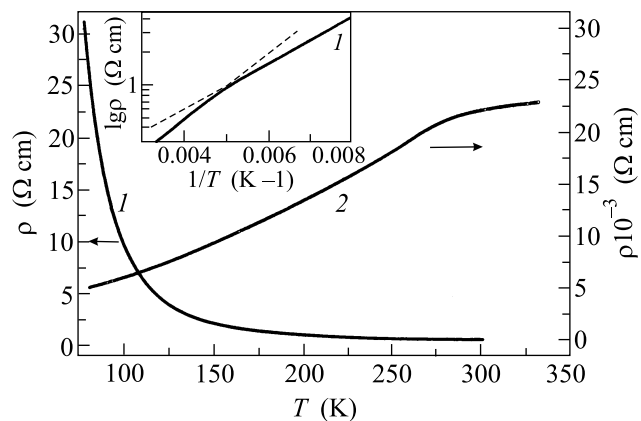


Fig.4. The temperature dependence of resistivity of CaCuMn₆O₁₂ (1) and CaCu₂Mn₅O₁₂ (2). The inset: the resistivity of CaCuMn₆O₁₂ in logarithmic scale versus inverse temperature

type, the ρ_2 vs. T dependence is of metallic type. The $\lg \rho_1$ vs. $1/T$ dependence in $\text{CaCuMn}_6\text{O}_{12}$, shown in the Inset to Fig.4, indicates that the activation energy for current carriers changes from 60 meV at $T > T_{C1}$ to 40 meV at $T < T_{C1}$. The magnetic phase transition at T_{C2} is well pronounced in ρ_2 vs. T dependence. Note, that the absolute values of resistivity of these compounds differ by several orders of magnitude.

Thus, the comparison of $\text{CaCuMn}_6\text{O}_{12}$ and $\text{CaCu}_2\text{Mn}_5\text{O}_{12}$ indicates that the compound with higher copper content possesses a higher Curie temperature and a lower saturation magnetization. Besides, these two compounds differ in the type of conductivity which is semiconducting in former compound and metallic in latter compound.

To treat these observations one has to consider the exchange interactions between the various magnetic ions in C and B positions and magnetic interactions within B position. The simplest situation is realized evidently in the parent compound of this family $\text{CaMn}_7\text{O}_{12}$ which orders predominantly antiferromagnetically at $T_N = 49$ K [14]. Taking into account rather low value of T_N one can assume that the magnetism in this compound is suppressed by weak overlap of the magnetoactive orbitals of $(\text{Mn}^{3+})_C$ and $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$ and by competition of superexchange and double exchange interactions of $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$.

The substitution of $(\text{Mn}^{3+})_C$ for $(\text{Cu}^{2+})_C$ leads to rapid increase of a ferromagnetic component in magnetization. Apparently, the strongest exchange interaction in $\text{Ca}(\text{Cu}_x\text{Mn}_{3-x})\text{Mn}_4\text{O}_{12}$ which dominates the magnetic behavior in these compounds is an antiferromagnetic interaction between $(\text{Cu}^{2+})_C$ and $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$ ions. This follows both from the existing experimental data [11,12] and from the ab-initio calculations [10]. The explanation of the strengths of this interaction follows directly from the crystal and electronic structure in these systems. For the Cu^{2+} ions in square coordination the active hole orbital is the $d_{x^2-y^2}$. This orbital has rather strong overlap with the p_x, p_y orbitals of the O^{2-} ions, which in turn overlap with d_{xz}, d_{yz} orbitals of t_{2g} manifold of $(\text{Mn})_B$ with the hopping matrix element $t_{pd\pi}$. The angle $(\text{Cu})_C - \text{O} - (\text{Mn})_B$ equal to 109° bond in $\text{CaCuMn}_6\text{O}_{12}$ and 110° bond in $\text{CaCu}_2\text{Mn}_5\text{O}_{12}$ is not far from 90° one. Thus, the exchange path gives rather strong antiferromagnetic coupling according to Goodenough – Kanamori – Anderson rules. It is very similar to $90^\circ t_{2g} - e_g$ exchange. One can estimate $J \sim t_{pd\sigma}^2 t_{pd\pi}^2 / \Delta^2 (\Delta + \Delta' + U_p)$, where Δ is the charge-transfer energy from oxygen to Mn or Cu (which is smaller), and Δ' is the charge – transfer energy to another ion (if Δ is O – Mn excitation, then Δ' is

that for O – Cu). All other exchange processes between C and B sites are smaller. In the compounds studied one should also discuss the $e_g - e_g$ exchange $(\text{Cu})_C - (\text{Mn}^{3+})_B$ as well as different contributions due to the pairs $(\text{Mn}^{3+})_C - (\text{Mn}^{3+}/\text{Mn}^{4+})_B$. It is difficult to calculate quantitatively these processes, since they depend on the type of e_g – occupation in $(\text{Mn}^{3+})_B$. Due to the almost square coordination of $(\text{Mn}^{3+})_C$ one can conclude that the electron at e_g – levels of $(\text{Mn}^{3+})_C$ would occupy the d_{z^2} orbital. In any case, such analysis shows that there are different contributions to the exchange $(\text{Mn}^{3+})_C - (\text{Mn}^{3+}/\text{Mn}^{4+})_B$, which have a tendency to cancel one another, so that the resulting exchange is difficult to predict, and one can expect it to be relatively small.

There remains the exchange interactions between $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$. Again, in a localized picture one would have different contributions: $t_{2g}-t_{2g}, t_{2g}-e_g, e_g-e_g$ which for the $\text{Mn}_B - \text{O} - \text{Mn}_B$ angle of about 142° (almost half-way between 180° and 90° exchange) are difficult to establish. The comparison with the situation in ferromagnetic pyrochlore manganite like $\text{Tl}_2\text{Mn}_2\text{O}_7$, in which the $\text{Mn} - \text{O} - \text{Mn}$ angle is comparable and all Mn are Mn^{4+} , shows that even $t_{2g}-t_{2g}$ exchange for this geometry may be ferromagnetic, all the more so e_g – contribution which would exist for $(\text{Mn}^{4+})_B - (\text{Mn}^{3+})_B$ pairs. Thus, in general we should expect ferromagnetic interactions in the B sublattice, even in a picture of localized electrons. But probably even more important is a ferromagnetic coupling within the B – sublattice due to the double exchange mechanism. Apparently, the systems considered are either metallic or at least small gap semiconductors, and their conductivity is definitely due to e_g -electron hopping through the $(\text{Mn})_B$ sublattice. It should be noted that the double exchange interaction may be not the main mechanism of ferro-, or rather ferrimagnetic behavior of these systems as argued by Zeng [5], it may even be antiferromagnetic. It is mainly the $(\text{Cu}^{2+})_C - (\text{Mn})_B$ antiferromagnetic superexchange which forces the spins of $(\text{Mn})_B$ ions to be parallel.

Thus, the resulting picture is the following: in $\text{Ca}(\text{Cu}_x\text{Mn}_{3-x})\text{Mn}_4\text{O}_{12}$ there exist a rather strong $(\text{Cu}^{2+})_C - (\text{Mn})_B$ antiferromagnetic exchange, and substantial ferromagnetic $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$ coupling. $(\text{Mn}^{3+})_C$ are coupled to $(\text{Mn}^{3+}/\text{Mn}^{4+})_B$ by much weaker interaction, the sign of which is difficult to determine. This treatment seems to be consistent with the main experimental observations: the spins of Cu sublattice are aligned antiparallel to those of $(\text{Mn})_B$, and $(\text{Mn})_C$ may be canted with respect to total magnetization in small fields [11,12]. The latter can be easily rotated to the direction parallel to the field and to

total magnetization (determined by (Mn)_B – sublattice) in relatively weak fields.

Apparently in CaCu₂Mn₅O₁₂ the saturation $M_s = 15 \mu_B/\text{f.u.}$ is reached already at low fields ~ 1 T, so that in this system either the spins of (Mn³⁺)_C are oriented parallel to the spins of (Mn)_B from the very beginning, or at least may have extremely weak coupling and easy to rotate.

In CaCuMn₆O₁₂ the magnetization quickly reaches the same value at low fields ~ 1 T, after which it slowly approaches saturation of about $20 \mu_B/\text{f.u.}$ Therefore, one can expect the gradual rotation of (Mn³⁺)_C spins in this system: there are more of them, and one can assume that their coupling to (Mn)_B is somewhat stronger. In any case, the magnetic field of about 45 T seems to be sufficient to orient magnetic moments of both types of Mn ferromagnetically, but definitely not enough to flip the Cu²⁺ spin, which remains antiparallel to the net magnetization. These considerations are consistent with the results of ab – initio calculations, where the antiferromagnetic exchange (Cu²⁺)_C – (Mn⁴⁺)_B was estimated to be 300 K [10].

In conclusion, it is found that two isostructural compounds of AC₃B₄O₁₂ family, namely CaCuMn₆O₁₂ and CaCu₂Mn₅O₁₂ possess drastically different thermodynamic and kinetic properties. The former compound is a semiconductor with basically non-collinear magnetic structure, while the latter compound is a metal with presumably collinear magnetic structure. The main role in magnetism of Cu – substituted double distorted manganites belongs to antiferromagnetic exchange interaction between (Cu²⁺)_C and (Mn³⁺/Mn⁴⁺)_B. This is because the magnetoactive e_g orbital of copper through oxygen p_x , p_y orbitals have strongest overlap with manifold of t_{2g} orbitals of manganese. The low values of coercive

force in these compounds provide rather high negative magnetoresistance in sponge ceramics due to intergranular tunneling in a wide temperature range.

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